

# METHOD FOR MANUFACTURING CATALYST BY USING SUPERCRITICAL FLUID AND CATALYST OBTAINED THEREBY

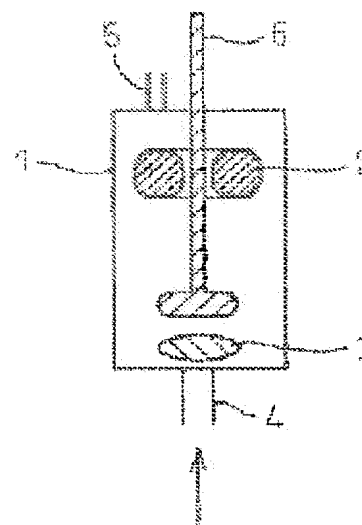
**Patentnummer:** JP2001224962 (A)  
**Publiceringsdato:** 2001-08-21  
**Opfinder(e):** HIRATA HIROTO; TSUJI SHINJI  
**Ansøger(e):** TOYOTA MOTOR CORP  
**Klassifikation:**  
 - international: B01D53/94; B01J23/42; B01J29/035; B01J29/44; B01J37/02; B01J37/03; B01D53/94; B01J23/42; B01J29/00; B01J37/00; (IPC1-7): B01J23/42; B01D53/94; B01J29/035; B01J29/44; B01J37/02; B01J37/03  
 - europæisk:  
**Ansøgningsnummer:** JP20000331244 20001030  
**Prioritetsnummer/-numre:** JP20000331244 20001030; JP19990346501 19991206

## Sammendrag af JP 2001224962 (A)

**PROBLEM TO BE SOLVED:** To provide a method for manufacturing a catalyst having high-degree uniformity of a catalytic component by depositing the catalytic component on a carrier having minute pores and to provide the catalyst having high-degree uniformity of the catalytic component deposited on the carrier. **SOLUTION:** This method for manufacturing the catalyst comprises contacting a supercritical fluid, in which a catalytic component raw material is dissolved, with the carrier to immobilize the catalytic component raw material on the carrier, preferably, by making good use of hydrolysis of the catalytic component raw material by the water adsorbed on the carrier.; In the concrete, the method comprises contacting the supercritical fluid such as CO<sub>2</sub> with the carrier such as meso-porous silica and  $\gamma$ -alumina in a pressure-resistance vessel, hydrolyzing the catalytic component raw material by the water adsorbed in the pores of the carrier to immobilize the catalytic component raw material on the carrier, releasing the supercritical state and firing the catalytic component raw material-immobilized carrier.

図 2

超臨界流体を用いた固定装置



JAPANESE [JP,2001-224962,A]

---

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE  
INVENTION TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS  
DRAWINGS

---

[Translation done.]

**\* NOTICES \***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

**TECHNICAL PROBLEM**

---

[Problem(s) to be Solved by the Invention]However, it is very difficult to fix a precious-metals drug solution uniformly in this adsorption or impregnation method over the whole surface, such as gamma-alumina with high specific surface area, and zeolite. Namely, such a precious-metals drug solution cannot arrive at the surface easily to the depths of fine pores, such as gamma-alumina with detailed unevenness, for example, It cannot reach easily to the inside of the fine pores in which zeolite etc. extend linearly, but there is a disposition that many precious-metals drug solutions are especially fixed by the neighborhood of an entrance of these fine pores.

[0005]For this reason, in the catalyst acquired, a shade arises in the holding amount of a catalyst component, and there is a problem that the catalyst component of utilization efficiency is low. The shade of this holding amount is considered to be one of the causes of sintering of the platinum particles under the high temperature atmosphere produced when a car is run continuously for a long time about the three way component catalyst which used platinum as the catalyst component, for example.

[0006]It also sets to develop a new catalyst, and since it is technically difficult to make detailed fine pores support a catalyst component, there is a problem that development of the catalyst using character, such as adsorption of fine pores, is barred. Therefore, an object of this invention is to provide the method of having homogeneity in the carrier which has detailed fine pores, and making it support a catalyst component highly, and the catalyst with which the catalyst component was supported by having homogeneity highly.

---

[Translation done.]

## \* NOTICES \*

JPD and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

**MEANS**


---

[Means for Solving the Problem]The above-mentioned purpose contacts supercritical fluid which dissolved a catalyst component raw material to a carrier, and is attained by a manufacturing method of a catalyst fixing a catalyst component to a carrier. That is, this invention is an invention which uses supercritical fluid for support of a catalyst component, has advanced homogeneity on the surface of [ whole ] a carrier, and makes a catalyst component support. Supercritical fluid provides a catalyst component raw material with high solubility and high diffusibility, and, thereby, this homogeneity depends them on the ability of a catalyst component raw material to reach with fixed concentration to the depths or an inside of fine pores.

[0008]According to a method of this invention, since a catalyst component has homogeneity highly and is supported, a catalyst with high utilization efficiency of a catalyst component can be provided. Since a catalyst with which a catalyst component was uniformly supported to an inside of very detailed fine pores is acquired, a catalyst which has effects, such as adsorption, and an effect of a catalyst component by the fine pores collectively can be provided.

[0009]

[Embodiment of the Invention]The supercritical fluid in particular used by this invention does not need to limit, and it is [ supercritical fluid ] usable in arbitrary supercritical fluid. For example, carbon dioxide, nitrous oxide, Freon 13, ethane, ethylene. It is usable in the supercritical fluid obtained under the conditions beyond critical temperature and the critical pressure peculiar to each as shown in drawing 1, such as propane, propylene, butane, hexane, methanol, ethanol, benzene, toluene, ammonia, and water. The ingredient which forms supercritical fluid may not be limited to single components, but may be a mixture. Here, carbon dioxide is preferably used from the ease of handling, and the field of cost.

[0010]It is usable in the arbitrary things which can provide a catalyst component and can be dissolved in the above-mentioned supercritical fluid as a catalyst component raw material. For example, the acetylacetonato expressed with chemical formula:  $(\text{CH}_3\text{COCHCOCH}_3)_p \text{Me}$ , Or a chemical formula : It is usable and the alkoxide etc. which are expressed with  $\text{Me}(\text{OC}_m\text{H}_{2m+1})_n$  here Me, they are Pt, Au, Pd, Rh, Si, aluminum, Zr, Ce, Ti, W, Ga, Mo, Nb, Sn, Hf, K, Na, Ca, Ba, etc. —  $p=1-4$  — it is  $m=1-4$  and  $n=1-5$  preferably.

[0011]Specifically Platinum acetyl acetate  $(\text{CH}_3\text{COCHCOCH}_3)_2 \text{Pt}$ , Palladium acetyl acetate  $(\text{CH}_3\text{COCHCOCH}_3)_2 \text{Pd}$ , Rhodium acetyl acetate  $(\text{CH}_3\text{COCHCOCH}_3)_3 \text{Rh}$ , Acetyl acetate like zirconium acetyl acetate  $(\text{CH}_3\text{COCHCOCH}_3)_3 \text{Zr}$ , An alkoxide like titanium propoxide  $\text{Ti}(\text{OC}_2\text{H}_5)_4$  and tungsten ethoxide  $\text{W}(\text{OC}_2\text{H}_5)_5$  is mentioned, in addition it is screw acetate triphenyl phosphate palladium.  $[(\text{C}_6\text{H}_5)_3\text{P}]$  It is usable in  ${}_2\text{Pd}(\text{O}_2\text{CCH}_3)_2$ , palladium acetate  $(\text{CH}_3\text{CO}_2)_2 \text{Pd}$ . etc.

[0012]The dissolution can be promoted by dissolving a catalyst component raw material in supercritical fluid being able to perform atmosphere in the resisting pressure container to which the catalyst component raw material was paid by only transposing to supercritical fluid, for example, and stirring supercritical fluid collectively using a mechanically agitating means. The "dissolution" of the catalyst component raw material as used in the field of this invention means

that the supercritical fluid having contained the catalyst component raw material is observed as one phase.

[0013]Here, time to exceed 10 hours depending on the combination of a catalyst component raw material and supercritical fluid, for example may be taken to dissolve a catalyst component raw material in supercritical fluid. In this case, the time which a process takes can be shortened by introducing the supercritical fluid which dissolved the catalyst component raw material in supercritical fluid beforehand within another pressure vessel, and dissolved the catalyst component raw material in the resisting pressure container into which the carrier was put from that resisting pressure container. When circulating continuously the resisting pressure container into which the carrier was put, and contacting the supercritical fluid which dissolved the catalyst component raw material also simplifies a process, it is effective.

[0014]Subsequently, a catalyst component raw material "is fixed" to a carrier by contacting the supercritical fluid which dissolved this catalyst component raw material to a carrier. Generally adsorption by ion operation of a carrier surface, etc., etc. can perform immobilization of this catalyst component raw material. In this case, by, introducing the supercritical fluid which dissolved the catalyst component raw material for example, in the resisting pressure container into which the carrier was put, and contacting that supercritical fluid to a carrier, Immobilization can be promoted by being able to fix to a carrier, combining a catalyst component raw material, and stirring supercritical fluid using a mechanically agitating means.

[0015]That is, after making the catalyst component raw material fix by adsorption etc. and removing supercritical fluid subsequently by contacting the supercritical fluid which dissolved catalyst component raw materials, such as the above acetyl acetate, on the surface of a carrier, a catalyst component raw material can be made to remain on that occasion.

[0016]Here, as a catalyst component raw material, it has hydrolysis nature, and if hydrolyzed, "immobilization" can be promoted by using what has the character which becomes insolubility for supercritical fluid. Without being accompanied to the supercritical fluid, after becoming insolubility on that spot and removing supercritical fluid subsequently, if it arrives at the surface of the carrier containing water, it can be stabilized and the catalyst component raw material which dissolved in supercritical fluid when the catalyst component raw material of such character was chosen can be made to fix on that occasion.

[0017]If gamma-alumina, zeolite, etc. are used as a carrier, since the compatibility over water is high, these by controlling the humidity appropriately beforehand if needed, Water can be adsorbed to the depths or the inside of fine pores, and it becomes possible to secure support of a catalyst component with more advanced homogeneity by using the water of adsorption. When it fixes a catalyst component using the water of adsorption of this carrier, it is appropriate that critical temperature uses the thing below 100 °C as supercritical fluid like carbon dioxide.

[0018]It is possible to also use as a carrier material like the gamma-alumina which has high specific surface area like about 180-m<sup>2</sup>/g, and has very detailed fine pores, and it to support a catalyst component with the method of using this supercritical fluid, uniformly. Although gamma-alumina has the high specific surface area applied to the surface by having very detailed unevenness, it is difficult to support a catalyst component with usual being impregnated to the depths of this unevenness.

[0019]It is possible to also use for an inside from the surface the material in which the fine pores of a very detailed diameter extend as a carrier, and to support a catalyst component with the method of using this supercritical fluid, uniformly. For example, fine pores with a diameter [ like mesoporous silica ] of 1-10 nm (nano meter) are the material which linear shape fine pores branch from the middle, and extends in three dimensions in one dimension [ linear shape ], and, specifically, they are zeolite MCM-41 and FSM-16 grade. The material which has these linear shape detailed fine pores is difficult to support a catalyst component with usual being impregnated to the inside of these fine pores.

[0020]Use supercritical fluid for such a carrier and it sets to support a catalyst component, If a carrier is made into gamma-alumina and a catalyst component is used as platinum of the precious metals, since platinum is uniformly supported on a carrier, the exhaust gas purifying

catalyst which has the high endurance by which sintering of the platinum particles under a high temperature atmosphere was controlled can be provided. If the zeolite which has detailed pore diameters, for example is made into a carrier and a catalyst component is made into palladium of the precious metals, The catalyst for exhaust gas purification which has the hydrocarbon adsorption performance and the hydrocarbon purification performance of palladium by the fine pores of zeolite collectively and which has high performance in purification of hydrocarbon in exhaust gas can be provided.

[0021]It can combine with such a catalyst component and a cocatalyst component can be supported with the method of this invention using supercritical fluid. This cocatalyst component is the alkaline metal or alkaline-earth metals which carries out occlusion of the  $\text{NO}_x$  in exhaust gas temporarily, and is a Ce-Zr multiple oxide suitable for purification of hydrocarbon in exhaust gas which has  $\text{O}_2$  storage performance, and there is by \*\* which promotes an operation of a catalyst component, for example. These cocatalyst components can use as a raw material the suitable compound chosen from above-mentioned acetylacetonato, an alkoxide, etc. like a catalyst component, and can support it to a carrier.

[0022]In order to fix such a catalyst component and cocatalyst component to a carrier, : Dissolve a catalyst component raw material and a cocatalyst component raw material in supercritical fluid, make a carrier contact as mentioned above, and fix a catalyst component raw material and a cocatalyst component raw material to a carrier together. Or it can also carry out by fixing cocatalyst component either one of a catalyst component raw material or a raw material to a carrier, and fixing the raw material of the other, after calcinating as follows and supporting.

[0023]Thus, subsequently the carrier to which the catalyst component raw material or the catalyst component raw material, and the cocatalyst component raw material were fixed is calcinated, and can support a catalyst component to a carrier. The catalyst component raw material fixed by contacting a carrier, When adsorption is fixed, are gestalten, such as acetylacetonato of a raw material, and when hydrolysis is fixed, may have a gestalt of hydroxide, and these, While using a final catalyst component and cocatalyst component according to this baking process, it can support firmly to a carrier. Although conditions, such as temperature at the time of this calcination and atmosphere, can be arbitrarily chosen according to the use of a catalyst component or a catalyst, generally they are performed under an oxidizing quality or a non-oxidizing atmosphere of 500-1000 \*\*.

---

[Translation done.]

**\* NOTICES \***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.\*\*\*\* shows the word which can not be translated.

3.In the drawings, any words are not translated.

---

**DESCRIPTION OF DRAWINGS**

---

[Brief Description of the Drawings]

[Drawing 1]It is a constitutional diagram of CO<sub>2</sub> showing the field which forms a supercritical state.

[Drawing 2]It is a schematic diagram of the device which supports a catalyst component raw material to a carrier using CO<sub>2</sub> of a supercritical state.

[Drawing 3]It is the graph which compared the initial purification performance of CH<sub>4</sub>.

[Drawing 4]It is the graph which compared the purification performance after the durability test of CH<sub>4</sub>.

[Drawing 5]It is a mimetic diagram which illustrates the structure of the catalyst of this invention.

[Description of Notations]

1 -- Resisting pressure container

2 -- Carrier

3 -- A catalyst component raw material or cocatalyst component raw material

4 -- Resisting pressure container entrance

5 -- Resisting pressure vessel outlet

6 -- Stirring wings

---

[Translation done.]

\* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.\*\*\* shows the word which can not be translated.

3.In the drawings, any words are not translated.

---

EXAMPLE

[Example]It explains with reference to example 1 drawing 2. 500-cc resisting pressure container (1) ~~Gamma-alumina powder~~ (specific surface area  $180\text{m}^2/\text{g}$ ) of the carrier which placed under room temperature atmospheric air of 80% of relative humidity beforehand for 24 hours and whose humidity was controlled to 2% of moisture regain, The ~~catalyst component raw material (platinum acetyl acetate)~~ corresponding to the noble metal amount shown in Table 1 was paid and sealed. Carrier (2) Gamma-alumina powder and catalyst component raw material (3) A position arranges a catalyst component raw material to the entrance (4) side of  $\text{CO}_2$  supercritical fluid, and is an exit (5). The carrier has been arranged to the side.

[0025]After heating this resisting pressure container to 80 \*\*, 80 \*\*  $\text{CO}_2$  was introduced into the resisting pressure container, pressure up was carried out to 40MPa, and the supercritical state was formed. This supercritical state is held for 4 hours, and they are stirring wings (6) about  $\text{CO}_2$  fluid in a meantime and resisting pressure container. It stirred mechanically.

Subsequently, after cooling a resisting pressure container to a room temperature, the ~~pressure was released and the sample of the gamma-alumina powder in which the catalyst component raw material was fixed was taken out~~. As a result of the chemical analysis, it was checked that platinum acetyl acetate is changing to platinum hydroxide, and platinum acetyl acetate was judged to be what was hydrolyzed by the water of adsorption of gamma-alumina powder.

[0026]This sample was calcinated under 500 \*\* atmospheric air in an electric furnace for 1 hour, and the catalyst of the gamma-alumina powder in which platinum was supported was acquired. The quantity of the catalyst component raw material which teaches this operation in a resisting pressure container was changed, and three kinds of catalysts were acquired (samples 1-3). It was checked as a result of transmission electron microscope observation (TEM) and an energy dispersion type spectroscopic analysis (EDX) that each catalyst of the samples 1-3 exists by thickness with platinum uniform to the depths of fine pores.

[0027]Example 2 -- this example shows the mode which introduces the supercritical fluid which the catalyst component raw material already dissolved into the resisting pressure container into which the carrier was put. The gamma-alumina powder (specific surface area  $180\text{m}^2/\text{g}$ ) of the carrier was put into the same resisting pressure container as having used in Example 1. Subsequently, the supercritical fluid of 40MPa was put in and sealed at 80 \*\* which the platinum acetyl acetate of the catalyst component raw material dissolved in the resisting pressure container, and it placed under the condition like Example 1 for 4 hours, stirring. The quantity of the catalyst component raw material in which supercritical fluid was made to dissolve this operation was changed, and three kinds of catalysts were acquired (samples 4-6).

[0028]Two kinds of catalysts (samples 7-8) were acquired like Example 2 except having replaced with the gamma-alumina powder of example 3 Example 2, and having used zeolite (ZSM5).

[0029]Example 4 -- this example shows the mode which supports a catalyst to the carrier by which the coat was carried out to the monolith made from cordierite. Replace with the gamma-alumina powder of Example 2, above gamma-alumina powder, zeolite (ZSM5), or these both put the 50-cc monolith made from cordierite by which the coat was carried out into a resisting pressure container, and it ranks second, The supercritical fluid of 80 \*\* and 40MPa which the



platinum acetyl acetate of the catalyst component raw material dissolved like Example 2 was introduced into the resisting pressure container, and three kinds of catalysts (samples 9-11) were acquired like Example 2.

[0030]the comparative example 1 -- this example shows the usual supporting method which does not use supercritical fluid. Tales doses of catalyst component raw materials (platinum acetyl acetate) to Example 1 were dissolved in organic solvent isopropyl alcohol, and in the solution, 50-cc gamma-alumina powder (specific surface area 180m<sup>2</sup>/g) was added, and it stirred under the ordinary pressure room temperature for 4 hours. Subsequently, after vacuum heating removed the organic solvent, like Example 1, it calcinated at 500 \*\* and the catalyst for comparison was acquired (samples 12-13).

[0031]- Evaluation (1)-each catalyst sample of catalyst performance was made into a pellet about 1 mm in diameter, and durable heat treatment of 1000 \*\*x 5 hours was performed for this pellet catalyst by the following model gas atmosphere (SUTOIKI).

Gas composition: 2000ppmCO+670ppmC<sub>3</sub>H<sub>8</sub>+1000ppmNO+3500ppmO<sub>2</sub>+14.7%CO<sub>2</sub>+10%H<sub>2</sub>O  
(emaider: N<sub>2</sub>)

[0032]The same model gas atmosphere (SUTOIKI) as 2 g of each of that pellet catalyst that carried out durable heat treatment was circulated by a part for 6-l./, and the temperature (the following "T50" is called.) which purifies C<sub>3</sub>H<sub>8</sub> 50% estimated. About the catalyst samples 9-11 of Example 4, it is in the state held on the monolith substrate, and these durable heat treatments and measurement of T50 were performed.

[0033]

[Table 1]

	試料	触媒組成		初期浄化性能 (℃)	耐久熱処理後 浄化性能 (℃)
		貴金屬	触媒担体		
実施例 1	1	Pt換算値で 1 wt%	γ Al <sub>2</sub> O <sub>3</sub> で 99wt%	2 5 1	3 1 5
	2	Pt換算値で 2 wt%	γ Al <sub>2</sub> O <sub>3</sub> で 98wt%	2 5 0	3 1 2
	3	Pt換算値で 10wt%	γ Al <sub>2</sub> O <sub>3</sub> で 90wt%	2 4 5	2 9 7
実施例 2	4	Pt換算値で 1 wt%	γ Al <sub>2</sub> O <sub>3</sub> で 99wt%	2 5 0	3 0 8
	5	Pt換算値で 2 wt%	γ Al <sub>2</sub> O <sub>3</sub> で 98wt%	2 4 8	3 0 3
	6	Pt換算値で 10wt%	γ Al <sub>2</sub> O <sub>3</sub> で 90wt%	2 4 1	3 0 0
実施例 3	7	Pt換算値で 2 wt%	ZSM5で 98wt%	2 3 1	2 9 8
	8	Pt換算値で 10wt%	ZSM5で 90wt%	2 2 3	3 0 2
実施例 4	9	Pt換算値で 2 wt%	γ Al <sub>2</sub> O <sub>3</sub> で 98wt%	2 4 7	3 1 3
	10	Pt換算値で 2 wt%	γ Al <sub>2</sub> O <sub>3</sub> + ZSM5 98wt%	2 4 4	2 8 1
	11	Pt換算値で 2 wt%	ZSM5で 98wt%	2 3 0	3 0 4
比較例	12	Pt換算値で 2 wt%	γ Al <sub>2</sub> O <sub>3</sub> で 98wt%	2 5 4	3 6 2
	13	Pt換算値で 2 wt%	ZSM5で 98wt%	2 3 4	4 0 5

[0034]From the evaluation result shown in Table 1, as for 11 kinds of catalysts of Examples 1-4, T50 after durable heat treatment is notably lower than the catalyst of the comparative example 1, and they understand clearly improvement in the durable performance by the support using supercritical fluid. The sample 2 of the same example of a platinum holding amount as the same carrier, the sample 5, and the sample 9, It turns out that the sample 12 of a comparative example

is contrasted, the sample 7 of an example, and the sample 11 and the sample 13 of a comparative example are contrasted, and all are excellent in the catalyst which the direction of the example acquired using supercritical fluid since T50 of the first stage was low also in initial purification performance.

[0035]It turns out that contrasting Example 1 and Example 2, dissolving a catalyst component raw material in supercritical fluid beforehand with another resisting pressure container, and making a carrier contact from T50 being equivalent does not have an adverse effect on catalyst performance at all. Since four Example T50 cannot be found as contrasted with Examples 1-3 as for inferiority, also where the coat of the carrier is carried out to MONORIRO, it turns out that it can apply the method of this invention.

[0036]Resisting pressure container (1) same with having used in example 5 Example 1 To inside, it is a carrier (2). Carry out and 30 g of mesoporous silica (FMS-16). Cocatalyst component raw material (3) It carries out and is 15.05 g of cerium (III) acetylacetonato and 3 hydrate and 14.95 g of zirconium (IV) acetylacetonato were put in (mole ratio of Ce/Zr=1/1), and 50 g of acetone was added and sealed as a solvent to this. CO<sub>2</sub> was introduced into this resisting pressure container, and it heated to 150 \*\*, and pressure up was carried out to 30MPa, the supercritical state was formed, and this state was held for 24 hours. Subsequently, after cooling a resisting pressure container to a room temperature, the pressure was released and the cocatalyst component raw material took out the mesoporous silica fixed inside fine pores.

[0037]This sample was calcinated under 600 \*\* atmospheric air in an electric furnace for 5 hours, and the mesoporous silica with which the Ce-Zr composite oxide layer was supported inside fine pores was obtained. It is a carrier (2) about this mesoporous silica. It returns to a position and is a pressure vessel (1). It is a catalyst component raw material (3) to inside. It carried out, 5.0 g of palladium (II) acetylacetonato was put in, and 50 g of acetone was added and sealed as a solvent to this.

[0038]Subsequently, CO<sub>2</sub> was introduced into this resisting pressure container, and it heated to 150 \*\*, and pressure up was carried out to 30MPa, the supercritical state was formed, and this state was held for 24 hours. Subsequently, after cooling a resisting pressure container to a room temperature, the Ce-Zr composite oxide layer support mesoporous silica which released the pressure and to which the catalyst component raw material was fixed was obtained. This sample was calcinated under 450 \*\* atmospheric air in an electric furnace for 2 hours, and the catalyst of this invention with which Pd and a Ce-Zr composite oxide layer were supported by mesoporous silica was acquired. 2.25 mass % Pd was contained in this catalyst as a result of ultimate analysis. It was observed as a result of analysis by TEM and EDX that the Ce-Zr composite oxide layer is formed to the inside of the fine pores of mesoporous silica by the thickness which is about 0.5-1 nm, and the inside of the fine pores is dotted with palladium with the particle diameter of about 1 nm.

[0039]It is made to be the same as that of Example 5 except having fixed the catalyst component raw material as it was, without performing a firing process to the next, after fixing example 6 cerium (III) acetylacetonato and 3 hydrate, and zirconium (IV) acetylacetonato, The catalyst of this invention with which Pd and a Ce-Zr composite oxide layer were supported by mesoporous silica was acquired. 2.61 mass % Pd was contained in this catalyst as a result of ultimate analysis.

[0040]The catalyst of this invention with which Pt and a Ce-Zr composite oxide layer were supported by mesoporous silica was acquired like Example 5 except having replaced with 5.0 g of palladium (II) acetylacetonato in example 7 Example 5, and having used 2.5 g of platinum (II) acetylacetonato. 2.63 mass % Pt was contained in this catalyst as a result of ultimate analysis.

[0041]The catalyst of this invention with which Pt and a Ce-Zr composite oxide layer were supported by mesoporous silica was acquired like Example 6 except having replaced with 5.0 g of palladium (II) acetylacetonato in example 8 Example 6, and having used 2.5 g of platinum (II) acetylacetonato. 3.03 mass % Pt was contained in this catalyst as a result of ultimate analysis.

[0042]15.05 g of cerium (III) in comparative example 2 Example 5 What dissolved acetylacetonato and 3 hydrate and 14.95 g of zirconium (IV) acetylacetonato in 50 g of acetone (mole ratio of

Ce/Zr=1/1) is evaporated to dryness as it is, This was calcinated under 600 \*\* atmospheric air in an electric furnace for 5 hours, and the powder of the Ce-Zr multiple oxide was obtained. This was impregnated so that the concentration of palladium might become 2.25 mass %, the palladium nitrate solution was calcinated at 450 \*\* to it for 2 hours, and the catalyst of the comparative example with which Pd was supported by the powder of the Ce-Zr multiple oxide was acquired.

[0043]The catalyst of the comparative example with which Pd was supported by the powder of the Ce-Zr multiple oxide was acquired like the comparative example 2 except having prepared so that the holding amount of comparative example 3 palladium might become 2.61 mass %.

[0044]A dinitrodiammine platinum nitric acid solution is used for the Ce-Zr multiple oxide (mole ratio of Ce/Zr=1/1) obtained like the comparative example 4 comparative example 2, Platinum was supported so that concentration might become 2.63 mass %, and it calcinated at 450 \*\* for 2 hours, and the catalyst of the comparative example with which Pt was supported by the powder of the Ce-Zr multiple oxide was acquired.

[0045]The catalyst of the comparative example with which Pt was supported by the powder of the Ce-Zr multiple oxide was acquired like the comparative example 4 except having prepared so that the concentration of comparative example 5 platinum might become 3.03 mass %.

[0046]- Make each catalyst sample of the evaluation (2)-examples 5-8 of catalyst performance, and the comparative examples 2-4 into a pellet about 2-3 mm in diameter, and it is 1.0 g each of this pellet catalyst The following gas composition (1) and (2) The durability test put for 8 hours under the 1000 \*\* atmosphere repeated a cycle for 2 minutes was presented.

Gas composition (1) : O+5% of 10%H<sub>2</sub>O<sub>2</sub> (emainder: N<sub>2</sub>)

Gas composition (2) : O+5% of 10%H<sub>2</sub>H<sub>2</sub> (emainder: N<sub>2</sub>)

[0047]The following model gas atmosphere was circulated by a part for 6-l./to 1.0 g each of the catalyst with which this durability test was presented, and the initial catalyst after preparation, and CH<sub>4</sub> measured the temperature T50 purified 50%.

Gas composition: 4000ppmCH<sub>4</sub>+400ppmNO+6.0%CO<sub>2</sub>+10%O<sub>2</sub>+10%H<sub>2</sub>O (emainder: N<sub>2</sub>)

T50 of CH<sub>4</sub> of the initial catalyst after this preparation and the catalyst after a durability test is shown in drawing 3 and drawing 4, respectively.

[0048]- As a result shows from the result of - drawing 3 and drawing 4, the catalyst of this invention understands that CH<sub>4</sub> purification performance is high for all after the first stage and durability. As for this reason, the fine pores of mesoporous silica adsorb CH<sub>4</sub>. Since the synergistic effect of the adsorbing action of fine pores and a catalysis that the catalyst component which exists in the inside of the fine pores promotes oxidation of the CH<sub>4</sub> was revealed, it thinks, and it is thought that it is based on the catalyst structure with which a catalyst component and a cocatalyst component coexist inside detailed fine pores.

[0049]Although drawing 5 is a strictly typical figure, it illustrates the state of coming to support catalyst components, such as palladium, and cocatalyst components, such as a Ce-Zr composite oxide layer, inside the fine pores of the mesoporous silica of this invention.

---

[Translation done.]

\* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

CLAIMS

---

[Claim(s)]

[Claim 1]A manufacturing method of a catalyst contacting supercritical fluid which dissolved a catalyst component raw material to a carrier, and fixing a catalyst component raw material to a carrier.

[Claim 2]A manufacturing method of the catalyst according to claim 1 which fixes a catalyst component raw material to a carrier in said contact using hydrolysis of a catalyst component raw material by water by which a carrier was adsorbed.

[Claim 3]A manufacturing method of the catalyst according to claim 1 or 2 using supercritical fluid of carbon dioxide.

[Claim 4]Within a resisting pressure container, contact supercritical fluid which dissolved a catalyst component raw material to a carrier, and by the water of adsorption within pore structure of a carrier, make a catalyst component raw material hydrolyze, this fixes a catalyst component raw material to a carrier, and it ranks second, A manufacturing method of a catalyst including each process of canceling a supercritical state and calcinating a carrier to which the catalyst component raw material was fixed.

[Claim 5]A manufacturing method of the catalyst according to claim 4 which introduces supercritical fluid which dissolved a catalyst component raw material into said resisting pressure container into which a carrier was put.

[Claim 6]A catalyst, wherein a carrier comes to support a catalyst component using supercritical fluid.

[Claim 7]A catalyst characterized by coming to support a catalyst component inside fine pores of mesoporous silica.

[Claim 8]A catalyst characterized by coming to support a catalyst component and a cocatalyst component of the precious metals inside fine pores of mesoporous silica.

[Claim 9]The catalyst according to claim 8 in which said cocatalyst component is a cerium zirconium multiple oxide.

[Claim 10]The catalyst according to any one of claims 7 to 9 acquired by a method according to any one of claims 1 to 5.

---

[Translation done.]